A Study on Colophony Resin.

A DISSERTATION

Submitted in Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University

BY

Hermann A. Loos, B.S., A.M.

EASTON, PA.:
THE CHEMICAL PUBLISHING COMPANY.
1900.

781
72L
CLASSED
ssertation

A Study on Colophony Resin.

A DISSERTATION

Submitted in Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University

BY

Hermann A. Loos, B.S., A.M.

EASTON, PA.:
THE CHEMICAL PUBLISHING COMPANY.
1900.

Digitized by the Internet Archive
in 2025

https://archive.org/details/studyoncolophony0000herm

TABLE OF CONTENTS.

PAGE.

Acknowledgment 4
Introduction 5

PART I.—Colophony Resin.

Sources of Colophony 6
Anhydride Structure of Colophony 6
Production of Anhydride by Melting Abietic Acid 10
Oxidation Products of Turpentine 11
Test for the Presence of Abietic Acid 11

PART II.—Preparation and Composition of Abietic Acid.

Historical Review of the Literature on Abietic Acid 12
Properties of Abietic Acid 18
Preparation of Pure Abietic Acid 20
Method of Trommsdorff, Maly, etc 21
"White Rosin" 21
"Black Rosin" 23
"Gum Thus" 24
Flückiger Method 25
"White Rosin" 25
"Black Rosin" 26
"Window Glass Rosin" 27
Direct Addition of Hydrochloric Acid 28
"White Rosin" 28
"Window Glass Rosin" 29
"Gum Thus" 30
Table of Analytical Results and Molecular Weight Determinations 31
Conclusion—Formula for Abietic Acid 31

PART III.—Salts of Abietic Acid.

Historical 33
Potassium Salt (Neutral) 34
Potassium Salt (Acid) 36
Sodium Salt (Neutral) 40
Sodium Salt (Acid) 40
Ammonium Salt 41
Other Salts 42
Effect of Hydrolization 42
Effect of Light 42
Resinate Colors 43
Conclusion 45
Biographical 46

ACKNOWLEDGMENT.

The author wishes to acknowledge his obligations to the officers of the chemical department who have aided him by friendly advice and counsel, and more especially to Prof. C. E. Pellew for the securing of samples and other necessary material, and to Mr. S. A. Tucker and Mr. M. T. Bogert for much valuable assistance during the pursuit of this work.

H. A. L.

INDUSTRIAL LABORATORY, HAVEMEYER HALL,
COLUMBIA UNIVERSITY.

INTRODUCTION.

In spite of the industrial importance of colophony resin, the nature of its constituents is not thoroughly understood and even the composition of its principal acid has long been a subject of controversy. Most of the work of a purely chemical nature has been directed toward the determination of a formula for abietic acid. The literature of the subject is full of contradictions and disparities of all sorts, and the following work has been undertaken with the hope of throwing some light on the disputed points and of determining the true composition of abietic acid by means of products of the greatest attainable purity. Much work has already been done with rosin, of an analytical and a technical nature; but this has been largely empirical, and it is probable that a better knowledge of the chemistry of this substance, and of the character of the salts it forms, will lead to many improvements in these directions.

The first part of this work is devoted to a discussion of the sources and constituents of crude colophony, together with some experimental work on the presence and formation of abietic anhydride, and the relation of the acid to the ordinary oxidation products of turpentine. An historical review is then given of the literature on abietic and other acids supposed present in colophony, and this is followed by a description of the experimental work done in preparing pure abeitic acid and determining its formula. The last part of the thesis is devoted to a description of the preparation and properties of some salts of this acid and of the changes they were noticed to undergo as the result of hydrolysis and the effect of sunlight.

PART I.

COLOPHONY RESIN.

The resins form a physiological class of solid and semifluid bodies, which result from constructive and destructive processes of plant life, and which show a great diversity in their physical and chemical properties. The most important resin, from an industrial point of view, is common rosin of colophony. This is obtained as a residue, from the natural resin as exhuded from the tree, by removing the turpentine with a steam distillation, and then keeping the product heated until all water has been removed, which is indicated by a clarification of the melt. This process influences greatly the color and general properties of the resulting rosin. Colophony is a vitreous, brittle substance, breaking with a conchoidal fracture; it is insoluble in water, but soluble in most organic solvents. It is almost odorless, and practically tasteless, and varies in color from a pale yellow to a dark brown. The various grades melt from 80°–100° and the specific gravity varies from 1.045 to 1.085.

In the United States the principal rosin-producing trees[1] are *Pinus palustris* (long-leaf pine), *P. taeda* (loblolly pine), and *P. cubensis* (Cuban pine). The principal European sources[2] are *P. laricio*, *P. pinaster*, *P. australis*, *P. taeda*, sometimes also *P. maritima*. In addition to these, other species sometimes furnish the commercial products sold as common rosin.

Colophony probably consists essentially of the anhydride of abietic acid, although many authorities have denied this. Flückiger showed that masses of freshly exhuded rosin which were clear and amorphous throughout gained in weight and assumed a crystalline structure when exposed to water or moist air. Other specimens, which were kept sealed and absolutely dry for two years, underwent no change in weight or structure. Maly obtained almost the calculated quantity of crystallizable acid from amorphous rosin by the action of dilute alcohol. In the following experiments by the author, the gain in weight

[1] Report U. S. Dept. of Agric., Div. of Forestry, 1891 and 1892.

[2] K. Dieterich: Anal. d. Harze, Balsame u. Gummiharze, p. 110.

approximates closely that required by the hydrolysis of abietic anhydride ($C_{38}H_{56}O_3$) to the free acid ($C_{19}H_{28}O_2$).

Some "White Rosin" was pulverized and dried over sulphuric acid in vacuum. Two portions were weighed in small weighing bottles, covered with 60 per cent. alcohol, and allowed to stand one week with frequent agitation. On carefully evaporating down, breaking up the mass, and drying alternately at 100°, and over sulphuric acid, the following changes in weight were noticed:

	A.	B.
Final weight	1.4919	1.9063
Original "	1.4512	1.8475
Gained "	0.0407	0.0588
Gained per cent.	2.8	3.18

Abietic anhydride (molecular weight = 558) requires an increase of 3.226 per cent. in weight to convert it to the free acid. Assuming 90 per cent. of abietic anhydride in this rosin, would require an increase in weight of 2.90 per cent.

Lewkowitsch,[1] on the other hand, says: "The high acid values, and especially the definite ether values, prove conclusively that colophony is not, as Maly maintains, an anhydride; *viz.*, abietic anhydride, but consists chiefly of free acids and small quantities of an anhydride." In the fourteen results he refers to, the difference between acid value and saponification[2] value, *i. e.*, the ether value, varies from 16.4 to 36.11. Amsel[3] finds the ether values in three determinations to be respectively 8, 7, and 7. Williams[4] also finds results which are, in general, lower than those mentioned by Lewkowitsch. This difference, it would seem, merely shows the presence of a small quantity of free acid in colophony, and this is amply accounted for by the partial hydrolysis the anhydride has undergone during the process of manufacture, or by the incomplete reversion to anhydride during the melting down process. Moreover, in

[1] "Com'l Anal. of Oils, Fats and Waxes," 2nd. ed., p. 235.

[2] According to K. Dieterich, it is erroneous to speak of "saponification" values in connection with rosin, since no ethers are present.

[3] Ztschr. angew Chem., 1896, p. 430.

[4] C. N., 58, p. 224.

the better grades of rosin in which the melting temperature has been kept lower, the acid figures are found to be higher, showing a greater proportion of free acid.

Perrenond,[1] V. Dietrich,[2] and Ducummun[3] hold that rosin contains the free acid, with no anhydride whatever. They base this view on the fact that crude rosin contains a smaller percentage of carbon than abietic acid does, while, as anhydride, it should contain a larger percentage. Abietic acid ($C_{19}H_{28}O_2$) contains 79.16 per cent. carbon, and the anhydride 81.7 per cent. Dietrich found 74 per cent. carbon in rosin, and 77.5 per cent. in the product obtained on melting abietic acid. An analysis of "White Rosin," made by the author, resulted as follows:

0.2185 gram substance gave 0.6070 gram CO_2 and 0.1848 gram water, which corresponds to

	Per cent.
C	75.75
H	9.40

It must not be forgotten, however, that other substances, such as terpenes and their oxidation products,[4] are always present in rosin, and these might tend to reduce the carbon content of the whole. The first crystallizations of abietic acid will, moreover, contain a smaller percentage of carbon than than the pure product, and even a small quantity of impurity will reduce the percentage of this constituent. A sample of abietic acid, prepared by Maly's method, gave, after the second crystallization, the following result on combustion:

0.2990 gram substance gave 0.5908 gram CO_2 and 0.1887 gram water, which equals

	Per cent.
C	77.11
H	10.03

As to molten abietic acid, it is well known that volatile

[1] C. Z., 1885 (IX), 1556, 1590.

[2] Inaugural Dissertation, Bern, 1883.

[3] Inaugural Dissertation, Bern, 1885.

[4] Terephthalic acid ($C_8H_6O_4$), an oxidation product of turpentine, contains 57.1 per cent carbon.

vapors are produced by its decomposition, consisting of terpenes, carbon dioxide, carbon monoxide, benzene hydrides, etc. The mere fact that less carbon is present shows that a decomposition has taken place, and this renders useless any comparison of carbon content.

Perrenond and his co-workers assume that colophony consists of crystals of abietic acid, imbedded in a resinous body. Crystals of this acid are very readily identified with the microscope; polarized light will always detect them, even in the presence of much amorphous matter. Wiesner[1] has shown that most natural resins (*i. e.*, such as are employed as removed from the tree, without melting or removing the turpentine by distillation) show crystals when examined in this way. He covered the particles of rosin with turpentine, or some solvent which dissolved the matrix to a greater extent than the crystals. This same treatment was applied by the author to all obtainable grades of commercial colophony, but in no case could any crystals be found; the smallest particles always presented merely the chonchoidal fracture, which is characteristic of most resins. Only in the case of "Gum Thus," which is a natural resin, could any crystals be detected. According to Wiesner, the clarification of the crude rosin on melting during the preparation of colophony is due to a reversion of the crystalline acid to anhydride. Lewkowitsch and Perrenond state that the anhydride does not form on melting abietic acid, and, in fact, the only definite anhydride that has been prepared artifically was made by Emmerling,[2] by heating the crystalline acid with hydriodic acid to 145.°

Some experiments were made with the object of determining, if possible, the changes produced in the crystalline acid by heating at various temperatures above its melting-point. Some pure acid was gently heated just above its melting-point. On cooling slowly, large crystals were seen to form in the melt, and when quite cold, a yellowish, opaque mass was left, which was crystalline throughout, as shown by a microscopical ex-

[1] Die technisch verwendeten Gummiarten Harze und Balsame, p. 114.

[2] Ber. d. chem. Ges., 12, 1441.

amination. As the temperature of the melt increases, more amorphous matter will be found on cooling. A product which has been cooled from 175°–180° will leave a perfectly amorphous vitreous mass, which has all the appearance of the original rosin, excepting that it is more brittle.[1] But it was found that that this mass could be crystallized directly from strong alcohol, which can not be done with colophony. The latter will leave an amorphous mass on evaporating a strong alcoholic solution, and will only crystallize after having been subjected to the hydrolyzing action of dilute alcohol, or strong alcohol with the addition of a mineral acid.

As already pointed out, analysis will give no indication of the presence of the anhydride, but the product obtained, as described, was decidedly different from the original colophony. Its transparent appearance was probably due to a solution of the free acid in some of the terpenes produced by the decomposition. Kraemer and Spilke[2] have shown that on heating rosin under pressure, the terpene $C_{18}H_{28}$ is formed according to the equation —

$$C_{19}H_{28}O_2 = C_{18}H_{28} + CO_2.$$

Some pure, dry abietic acid was heated for two hours at 180°–195°; water and other vapors were given off. On cooling, a brown vitreous mass was left. A saturated solution of this product in alcohol did not crystallize, even on standing several days. On the other hand, portions treated with dilute alcohol or hydrochloric acid gave crystals of abietic acid in a few hours. This product resembled, in all respects, the colophony from which the abietic acid had been originally made. This would indicate that some anhydride is formed by a continued heating at this temperature.

Abietic acid has often been considered an oxidation-product of turpentine. Terpenes contain no oxygen; all resins do; hence it has been thought that the resins are oxidation-products of the terpenes. But in no case has it been possible to

[1] When a shallow layer of melted abietic acid is allowed to cool, it will contract and suddenly crack up into small pieces, with a distinctly audible decrepitation.

[2] Ber. d. chem. Ges., 1899, pp. 2952 and 3614.

produce any of the known resins by oxidation of a balsam or essential oil, nor has the reverse process been possible ; *i. e.*, the reduction of a resin to a known terpene. Resinous bodies of some kind do, however, form by oxidation of essential oils and there seems to be a loss of hydrogen in this process. Heldt[1] claimed that resins are formed by a simple oxidation of ethereal oils, there being a direct addition of oxygen and loss of hydrogen in the form of water. Perrenond and Ducummun deny the identity of abietic acid with the resin produced by oxidizing terpentine. They examined turpentine that had been treated with ozone and some that had resinified on standing several years, but in no case could any color reaction be obtained for abietic acid. The only product that could be identified was terephthalic acid.

Some experiments made by the author gave no better results. An old sample of turpentine, which was known to have stood for five or six years, was distilled with steam ; the residue was washed with alkali and these washings were precipitated with acid. No indication of abietic acid could be obtained. Samples of terpentine were oxidized with hydrogen peroxide and sodium peroxide. Especially with the latter reagent, the oxidation was very violent. The excess of turpentine was now distilled off with steam and the residue examined. No crystalline product could be prepared from it, nor did any of the tests for abietic acid indicate its presence. One of the tests employed was based on the fact that abietic acid will give colored lakes with an aniline dye ; *i. e.*, a double salt of metal and a basic color seems to form (see p. 43 of this thesis). The solubility of this substance in benzol serves as an indication of its presence. The above oxidation-products were treated with dilute alkali ; methyl violet was added and then zinc sulphate. A small precipitate formed, but this, when dried and treated with benzol, gave no colored solution.

In the preparation of abietic acid from rosin a yield of 80–95 per cent. of crude acid is obtained.[1] More of the acid will

[1] Ann. Chem. (Liebig), 63, 18.

[2] In one case Mach obtained 98 per cent. of crude acid from a sample of French colophony.

slowly crystallize out from the mother-liquor, during several months' standing.[1] No other acids, crystalline or amorphous, have been separated from the mother-liquors. The amorphous acids which are often described in colophony consist mainly of abietic acid which is held back in the mother-liquors. A small quantity of turpentine and its oxidation-products, some of which are acid in character, are also present. Colophony also contains terpenes and other decomposition-products produced by the breaking up of the abietic acid at the temperature required to drive off the last traces of water in the process of its manufacture.

PART II.

ABIETIC ACID: HISTORY, PREPARATION, AND COMPOSITION.

Previous to 1825, Ries,[2] in Vienna, obtained some crystalline bodies by acting on white pitch with acids. No analyses nor attempts at identification were made. In 1826 Baup[3] separated a crystalline body from the resin of *P. abies* and named it "acide abietique"; a similar body from Bordeaux resin (probably *P. maritima*) he named "acide pinique" (apparently identical with pimaric acid of Laurent). Unverdorben[4] showed the acid character of colophony and described several of its salts. On precipitating an alkali salt with acid he observed an increase in weight which he ascribed to the formation of a hydrate.[5] He described three acid bodies in ordinary resins which he named respectively α-, β-, and γ-resin. In colophony he describes seven constituents, the principal ones being "Sylvinsäure" (α-resin), a crystalline body which he declares is identical with that obtained by Ries. An amorphous

[1] If the mother-liquor is stirred with a glass rod and then allowed to stand several weeks the crystals will separate on the sides where touched by the rod, very much like a precipitate of magnesium phosphate will.

[2] Jahrbuch d. Polytech. Inst. zu Wien, I., p. 435; Repert. d. organ. Chem. v. Fechner, p. 1291.

[3] Ann. chim. phys., 31, 108.

[4] Pogg. Ann., 7, 311; 8, 405.

[5] *Ibid.*, 11, 27, 230, 393.

body (β-resin) which he named "Pininsäure" and a deeply-colored substance, "colopholsäure", which is the result of superheating pininsäure." He describes other constituents of rosin and salts of the acids but gives no analyses. Trommsdorff[1] prepared the crystalline acid by treating rosin with 60 per cent. alcohol, and on the strength of his analysis concludes that it is an oxidation-product, not of temperature but of a radical $C_{10}H_{15}$, having one hydrogen atom less. He gives this acid the formula $C_{40}H_{60}O_4$,[2] based on the composition of the copper salt. Rose[3] agrees with this formula but adds that colophony is an oxidation-product of turpentine.

Caillot[4] found an acid in Strasburg turpentine which he called "abiesinsäure" and which was subsequently believed to be a mixture of sylvinic acid and pimaric acid. Laurent[5] believed this acid to be different from sylvic and to be identical with the one he obtained from Colophonium du Bordeaux (*P. maritima*)and he accordingly gave it the name "Pimarsäure." This body had, however, the same composition as sylvic and pinic acid ; on distillation it formed pyromaric acid. Strecker[6] subsequently suggests the identity of pyromaric, pimaric, sylvic and, in fact, all the acids obtained from American colophony. Caillot[7] again took up the work and agrees with Laurent on a melting-point of 125° for pimaric acid. He found it to be laevo-rotatory and when heated to 100° it changed to a dextro-rotatory acid, which melted at 208°.

Siewert[8] declares that abietic acid is isomeric with pimaric but differs from it in being slightly more soluble in alcohol. He succeeded in obtaining a crystalline potassium salt of the composition $C_{20}H_{29}KO_2$, $3C_{20}H_{30}O_2$.

[1] Ann. Chem. (Liebig), 13, 169.

[2] In this case and wherever necessary, formulas and analyses based on the old carbon equivalent have been changed and recalculated.

[3] Ann. Chem. (Liebig), 13, 174.

[4] J. de Ph. et. de Ch., 16, 436; Bull. Soc. Chim. (Paris), 21², 387; and Ber. d. chem. Ges., 7, 484.

[5] Ann. Chem. (Liebig), 34, 272; Ann. chim. phys., 72, 383.

[6] Ann. Chem. Pharm., 68, 338; Ann. Chem. (Liebig), 150, 131.

[7] Ber. d. chem. Ges., 7, 484.

[8] Jsb. d. Chem., I, p. 572; and XII, p. 508.

Maly[1] prepared an acid from American colophony by the method of Trommsdorff and Unverdorben. He could get no crystalline potassium salt and hence claimed that Siewert's acid was different from his, which he called abietic acid. He retains the name "sylvinsäure" for the acid produced from colophony by the action of hydrochloric or other mineral acids and shows that no ether is formed when dry hydrochloric acid gas acts on a solution of abietic acid in strong alcohol. Maly considers abietic acid to be dibasic and gives it a new formula; *viz.*, $C_{44}H_{64}O_6$. He prepared an ethyl and a glyceryl ester and made a series of interesting hydrocarbons by the action of phosphorus pentachloride. By the action of sodium amalgam he obtained a body which he called hydro-abietic acid but which shows no definite distinction from abietic acid itself.

Duvernoy[2] and Strecker[3] take exception to Maly's formula for abietic acid and declare Siewert's formula, $C_{20}H_{30}O_2$, to be the correct one. Strecker declares abietic and silvic acids to be identical. Duvernoy obtained a crystalline lead salt from this acid which removed a supposed distinction between it and pimaric acid. He also obtained a crystalline sodium salt, and an acid, and a neutral salt of potassium, but could get no crystalline salt of ammonium with abietic acid, and considered this a distinction from pimaric acid. Maly[4] maintains the identity of pimaric and abietic acids, and finally admits that while the latter has the formula $C_{44}H_{64}O_6$ there is also a small quantity of the $C_{20}H_{30}O_2$ acid present in colophony.

Flückiger[5] led dry hydrochloric acid gas into an alcoholic solution of rosin and obtained a body which was shown to be identical with abietic acid, although Maly had claimed that this would give an entirely different acid. Emmerling[6] pre-

[1] Maly: Jsb. d Chem., 1861, p. 389; J. prakt. Chem., **86**, 111; *Ibid.*, **92**, 1; *Ibid.*, **96**, 145; Ann. Chem. (Liebig), **149**, 244; *Ibid.*, **161**, 115; Chem. Centrbl., 3, 59; Sitzungsber. d. Wien. Acad., 44 (II), 128; 48 (II), 355; 50 (II).

[2] Inaugural Diss., Tübingen, 1865; Ann. Chem. (Liebig), **148**, 143.

[3] *Ibid.*, **150**, 131.

[4] *Ibid.*, **149**, 244.

[5] J. prakt. Chem., **131**, 235.

[6] Ber. d. chem. Ges., **12**, 1441.

pared the acid by various methods and concluded that Flückiger's acid is identical with abietic ; his analytical results on the free acid and the salt agree with Maly's formula, $C_{44}H_{64}O_5$. Emmerling prepared a bromine derivative and an impure acetyl derivative, studied the action of hydriodic acid, of oxidizing agents, of fused caustic potash and prepared a series of hydrocarbons by a zinc chloride distillation. Kelbe,[1] while at work on a process of purifying rosin oil, succeeded in preparing abietic acid from this substance ; he also retains Maly's formula. Liebermann[2] admits the identity of abietic and sylvic acids and declares them to have the same composition as pimaric acid, $C_{20}H_{30}O_2$. He obtained a series of hydrocarbons by acting on these acids with hydriodic acid and red phosphorus and found that they rotated the plane of polarization in opposite directions. Haller[3] confirmed this work, gave some analyses of abietic acid, and determined its rotation to be $[\alpha]_D = -53°$.

Valente[4] separated a crystalline body from colophony, which, while still in a crude condition, gave a melting-point of 165° and turned the plane of polarization to the right. He made it from Bordeaux resin and although he calls it sylvic acid he evidently had in hand the pimaric acid of Laurent. His analyses agree with the formula $C_{20}H_{30}O_2$ and he concludes that Maly's acid does not exist and that Liebermann based his examination on a mixture and not a pure substance. Perrenond[5] and his co-workers, V. Dietrich[6] and Ducummun,[7] next took up this work. Dietrich examined American and European resins and found abietic acid in the former and pimaric acid in the latter. These acids he found to agree in composition but to differ in melting-point and rotatory power (see table,

[1] Ber. d. chem. Ges., 11, 2174 ; *Ibid.*, 13, 888.

[2] *Ibid.*, 17, 1885.

[3] *Ibid.*, 18, 2165.

[4] Atti della Reale Acc. dei Lincei, I, 13, 1884 ; Ber. d. chem. Ges., 18 (3), 190.

[5] Chem. Ztg., 9, 1590.

[6] Étude comparée sur l'acide abietique et l'acide pimarique (1883), Bern.

[7] Étude sur les acides crystallisables des Abitinées (1885), Bern.

p. 19); both are said to have the composition of an oxy-cymol, $C_{10}H_{14}O$, although the analyses given differ considerably from the theoretical requirements (see table, p. 18).

Based on the composition of the ammonium salt the formula of pimaric acid is given as $4(C_{10}H_{14}O)$. Abietic acid, according to these authors, gives no crystalline ammonium salt but merely a gelatinous soap. Ducummun found abietic acid in the root resin of *P. sylvestris* and pimaric acid in the trunk resin of the same tree.

Vesterberg[1] finally showed pimaric acid to be distinctly different from abietic acid. He obtained from French galipot resin, three isomeric acids; the first is dextro-pimaric, which melts at 210°–211° and has a rotation of $[\alpha]_D = +59°.2$; the second, laevo-pimaric, melts at 140°–150°, and has a rotation of $[\alpha]_D = -272°$. His analyses agree well with the formula $C_{20}H_{30}O_2$ (see table, p. 18).

Mach, a pupil of Maly, gives a new formula for abietic acid; *viz.*, $C_{19}H_{28}O_2$. He obtained a product of great purity from several species of American colophony and his analyses average 78.97 per cent. carbon and 9.84 per cent. hydrogen; the formula he proposes calls for 79.16 per cent. carbon and 9.73 per cent. hydrogen. The distinctive feature of Mach's work, however, is the rational step he took in making a series of molecular weight determinations by Beckmann's method. His results vary from 269 to 344. This at once excludes Maly's formula, which requires a molecular weight of 672. Mach's formula calls for a molecular weight of 288, and seven determinations made with dilute solutions (which, as is well known, give more accurate results in this method) vary from 269 to 298, and average at 285.5. It is clearly seen that these results, as well as the analytical data, agree very closely with the formula he proposes.

Mach's formula has, however, not been universally accepted. In view of the great disparity in the work done on this substance, as pointed out in the preceding pages, the following work was undertaken with the hope of throwing some light on these much disputed points.

[1] Ber. d. chem. Ges., 18, 3331; *Ibid.*, 19, 2167; *Ibid.*, 20, 3248.

Table of Published Analyses of Abietic and Pimaric Acids.

Abietic Acid.

	C. Per cent.	H. Per cent.
Trommsdorff	78.21	9.86
	78.54	9.79
Liebig	78.65	9.82
Rose	77.12	9.42
	75.19	9.46
	76.81	9.36
	76.63	9.27
	76.21	9.43
	76.93	9.64
	78.19	9.95
	78.92	9.97
Siewert	79.12	9.68
	79.50	9.85
	79.00	9.63
	79.93	9.63
Maly	78.69	10.00
	78.66	9.97
	78.53	9.75
	78.54	9.72
Kraut[1]	78.37	9.68
Emmerling	78.74	9.68
	78.62	9.59
	78.42	9.64
Kelbe	78.64	10.00
Haller	78.85	9.78
	78.65	9.62
V. Dietrich	79.32	9.63
Ducummun	79.28	9.72
	79.47	9.56
	79.15	9.58
	79.26	9.62
	79.34	9.64
	79.36	9.65
Mach	78.89	9.81
	78.94	9.86
	78.88	9.81
	78.92	9.84

Abietic Acid (continued).

	C. Per cent.	H. Per cent.
	78.93	9.85
	78.90	9.82
	78.95	9.86
	79.07	9.84
	79.02	9.84
	78.91	9.89
	78.78	9.92
	78.83	9.84
	78.99	9.83
	78.62	9.74
Theory for $C_{19}H_{28}O_2$	79.16	9.73

Pimaric Acid.

	C. Per cent.	H. Per cent.
Laurent	78.18	9.74
Haller	78.47	9.41
	78.62	9.62
Duvernoy	79.23	9.95
	79.12	10.00
V. Dietrich	79.46	9.63
Ducummun	79.45	9.68
	79.60	9.60
	79.02	9.52
Vesterberg	79.28	9.96
	79.29	10.64
	79.26	10.16
Mach	79.33	10.00
Theory for $C_{20}H_{30}O_2$	79.47	9.94

CHEMICAL AND PHYSICAL PROPERTIES OF ABIETIC ACID.

Pure abietic acid is a white crystalline body insoluble in water and soluble in most organic solvents. A table of solubilities is given on p. 22. The crystalline structure has been studied by Siewert,[1] Lang,[2] Wulf,[3] Fock,[4] and Graber.[5]

[1] Zeit. für die gesam. naturwissenschaften, Giebel u. Heintz, 14, 311.

[2] J. prakt. Chem., 96, 164.

[3] Ber. d. chem. Ges., 13, 888.

[4] Groth's Zeit. für Krystallographie, 1883, VII, p. 58.

[5] Monatsh. Chem., 15, 628.

Abietic acid is optically active both in the crystalline form and in solution. Some of the observed rotations for abietic acid are :

Valente: $[\alpha]_D$	$= \pm 37.87$	
Haller	$= -53°$	
Mach	$= -56.97$	(Abietic of a m. p. = 153°–154°.
	$= -67.34$	(After an additional crystallization.)
	$= -66.94$	
	$= -66.66$	(After three additional crystallizations.)
	$= -69.96$	(French colophony, 14th crystallization.)

The melting-point of abietic acid was found in the following work to be 159°–161°, but was never sharp. Mach found that all his products melted sharply at 153°–154°. The melting-points recorded by different observers vary greatly, as is seen in the table here given ; those of pimaric acid are also given for comparison :

	Abietic Acid. [Sylvic acid.]
Siewert	162°
Maly	165°
Flückig	120° (Soft) 135° (Melted)
Duvernoy	129°
Kelbe	165°
Emmerling	139°
Haller	145° (Soft) 161°–2° (Melted)
Dietrich	165°
Mach	153°–154°
	Pimaric Acid.
Laurent	125°
Caillot	125° 208° (Dextropimaric)
Siewert	155°
Maly	165°
Duvernoy	149°
Haller	120° (Soft) 149° (Melted)
Dietrich	148°
Vesterberg	210°–211° (Dextropimaric) 140°–150° (Laevopimaric)

Preparation of Pure Abietic Acid and Determination of its Formula.

There have been proposed six formulae for abietic acid. The analyses on which they are based show, as a rule, great variation. Rose's determinations of carbon content vary from 75.19 to 78.92 per cent.[1] Mach pointed out that impure abietic acid will give a lower carbon content and will approach in this respect the results obtained by earlier observers.

In the following work abietic acid was prepared by different methods from three typical grades of American colophony and also from a natural resin from *Pinus palustris* (the long-leaf pine) one of the chief rosin-producing trees in this country. The crystalline products were shown to be identical by microscopical examination, ultimate analysis, and determination of molecular weight. The analytical results agree closely with those obtained by Siewert[1] and Mach and confirm in all respects the formula proposed by the latter; *i. e.*, $C_{19}H_{28}O_2$.

Abietic acid will not crystallize directly from a solution of rosin; on evaporating a solution in alcohol, ether, chloroform, benzol, or petroleum ether, an amorphous mass remains. Rosin consists essentially of abietic anhydride, and this must first be hydrolyzed to the free acid before crystallization can take place. On saponifying rosin with alkali and then precipitating with a mineral acid, free abietic acid is obtained but is contaminated with much amorphous matter and is in a condition from which it can be crystallized only with the greatest difficulty. This is due to the fact that terpenes and other by-products originally present are dissolved to some extent in the rosin soap and are subsequently precipitated mechanically with the abietic acid.

There are two general methods of preparation. The first is the method of Trommsdorff in which the hydrolysis is pro-

[1] Although Siewert proposes the formula $C_{20}H_{30}O_2$ his analytical results agree more closely with $C_{19}H_{28}O_2$.

Four analyses given by Siewert average 79.14 per cent. carbon and 9.70 per cent. hydrogen.

$C_{19}H_{28}O_2$ requires 79.16 per cent. carbon and 9.73 per cent. hydrogen.

$C_{20}H_{30}O_2$ requires 79.47 per cent. carbon and 9.94 per cent. hydrogen.

duced by the aid of dilute alcohol, which brings the rosin particles into intimate contact with water. In the second, the method of Flückiger, the anhydride is changed to free acid by passing a stream of dry hydrochloric acid gas into an alcoholic solution of rosin. This method may be modified by adding small quantities of mineral acid directly to such solution. Mechanical devices such as pressure, suction filters, and centrifugals are indispensable for removing amorphous matter from the crystalline products. As solvents for recrystallization, methyl or ethyl alcohol, ether, petroleum ether, acetic acid, or benzol may be used.

Method of Trommsdorff, Maly, Etc.

Portions of 100 grams "white rosin" were pulverized and digested repeatedly with 70 per cent. alcohol. A brown, viscous layer settled on the bottom of the receptacle, and above this a white flocculent layer slowly formed. After standing two to three weeks the entire mass became granular. Frequent trituration of this mass in a mortar was found to hasten the separation. It was now filtered with suction or pressure and dried below 100°. This substance, when examined under the microscope with polarized light, appears distinctly crystalline in character but much amorphous matter is still present. The melting-point of a portion dried in vacuum over sulphuric acid was 102°–105°. If the original product was not finely ground the melting-point was always 3°–4° lower. The product was again digested with dilute alcohol and filtered by means of suction. It was now dissolved in hot 95.5 per cent. alcohol, diluted with water to beginning of turbidity, and allowed to cool; an oily layer separated which became granular in about twenty-four hours. This was filtered and again crystallized; only after this process had been repeated four or five times could good crystals be obtained, though they were still deeply colored. The amorphous residue contaminated all crystallizations with the greatest pertinacity. To determine the best medium for removing it, the combined mother-liquors were diluted, the separated substance dried over sulphuric acid, and its solubility then compared with that of abietic acid. Satura-

ted solutions of abietic and the amorphous residue at 23° C. were found to contain the following percentages of their weight of substance :

	Abietic acid. Per cent.	Amorphous residue. Per cent.
Absolute alcohol	18.7	23.7
95.5 per cent. alcohol	10.23	16.6
70 " "	1.2	15.9
Equal parts 95.5 per cent alchol and ether	37.9	38.2
Ether	37.8	39.7
Methyl alcohol	8.5	35.5
Benzol	61.1	22.5

In accordance with these results, dilute alcohol was used for the first crystallizations (*i. e.*, a hot solution of the substance in strong alcohol was diluted), and methyl alcohol for the final ones, since this medium was found to give much better crystals. If about one per cent. of water by volume is added to a methyl alcohol solution of abietic acid, crystals from 6–8 mm. across can sometimes be obtained. Glacial acetic acid has been suggested as a crystallizing medium.[1] This was found, however, to give good crystals only when but little amorphous matter was present ; *i. e.*, with a product that had already been purified. In this case large crystals may be obtained ; if allowed to stand in the mother-liquor for a few days, however, they will again go into solution probably with the formation of some acetyl derivative. The addition of water will again precipitate abietic acid.

The above product, purified as described, gave a higher melting-point with each crystallization, until after the fourteenth it melted at 154°–160°. It was tinted slightly yellow. An additional crystallization gave no improvement in color nor rise in melting-point.

Two analyses of this product gave the following results :

0.2007 gram substance gave 0.1776 gram H_2O, and 0.5802 gram CO_2, corresponding to

	Per cent.
Carbon	78.83
Hydrogen	9.83

[1] Kelbe : Ber. d. chem. Ges., 13, 888.

0.2344 gram substance gave 0.2045 gram H_2O, and 0.6782 gram CO_2, corresponding to

	Per cent.
Carbon	78.91
Hydrogen	9.70

A molecular weight determination made by the boiling-point method, in a Beckmann apparatus, gave the following result ($K = 2530$) :

0.2914 gram substance, dissolved in 31.252 grams acetic acid, raised the boiling-point 0°.086, which corresponds to a molecular weight of 274.

A determination by the freezing-point method, in a Raoult apparatus, gave the following result ($K = 3880$) :

0.6916 gram substance, in 21.783 grams glacial acetic acid, lowered the freezing-point 0°.406, corresponding to $\mu = 303$.

This method of preparation was laborious and time-consuming and required large quantities of solvents. The melting-point, as in the products from other methods of preparation, was not sharp, probably due to decomposition beginning in the vicinity of the melting-point. This product was also found to have retained a slight quantity of impurity by the benzol and hydrochloric acid test described on page 28.

The same process was now applied to some "black rosin." This is a crude product of very dark color ; it is prepared from the poorest quality of turpentine and consists mainly of the residues from the turpentine stills. It is sometimes sold as American galipot rosin but must not be confused with the French galipot, from which it is entirely distinct. The difficulties of this method of preparation were simply manifolded with this rosin. Fifty grams were pulverized and digested with 200 cubic centimeters of 70 per cent. alcohol. After standing ten days the mass was pressed, washed, and again treated with alcohol of the same strength. The product was now crystallized fifteen times,[1] first from ethyl and finally from methyl

[1] In making these crystallizations the product was dissolved in strong alcohol with heat, diluted with cold water just to turbidity, cooled rapidly with occasional shaking, allowed to stand one hour, filtered with suction nntil almost dry, and then redissolved in strong alcohol. Each crystallization was also washed with small quantities of 70 per cent. alcohol.

alcohol. It now melted between 149°–154°, was crystalline in character but yellowish in color. The hydrochloric acid and benzol test showed this product to be impure. No further crystallizations were made.

0.2227 gram of the substance, dried over sulphuric acid in vacuum, gave on analysis 0.1977 gram H_2O, and 0.6426 gram CO_2, corresponding to

	Per cent.
Hydrogen	9.86
Carbon	78.66

While this method is very troublesome when applied to manufactured rosins (such as have been subjected to distillation and subsequent melting down), it was found very satisfactory for the treatment of a natural rosin. For this purpose, what is commonly known as "Gum Thus," or crude turpentine,[1] was used. This is an exhudation of the *Pinus palustris*: it is a soft, yellowish, opaque resin of decided turpentine odor, containing 17 per cent. of volatile oil.[2] The opacity is due to the presence of some free abietic acid (produced from the anhydride by the action of moist air); a strong alcohol solution will deposit this constituent in the form of a crystalline layer on standing over night. The resin was pulverized, and 50 grams were shaken up with 250 cubic centimeters of 70 per cent. alcohol. After standing four days, the mass was pressed, washed twice with dilute alcohol, and recrystallized. Four additional crystallizations were made. The product now melted at 159°–161°, and gave the following results on analysis: 0.2884 gram substance gave 0.2562 gram water and 0.8975 gram CO_2, which corresponds to

	Per cent.
Hydrogen	9.87
Carbon	78.98

Determination of molecular weight by the boiling-point method:

0.3495 gram substance dissolved in 18.070 grams absolute

[1] Other synonyms are: Thus Americanum, Terebinthina, Common Frankincense.

[2] U. S. Dispensatory, 1894, p. 1356.

ether caused a lowering of 0°.150 in the boiling-point, corresponding to a molecular weight of 272.

Use of Acids to Aid Hydrolisation.

Flückiger's[1] method consists in passing hydrochloric acid gas into an alcoholic solution of rosin; he dissolved the rosin in seven times its weight of 70 per cent. alcohol, and then passed the dry gas. Maly thought that the action of hydrochloric acid formed a new acid distinct from abietic, which he called "Sylvinolsäure." Mach, however, showed that the product obtained in this way is identical with abietic acid. He passed dry hydrochloric acid gas into a very concentrated solution of rosin in 95.5 per cent. alcohol until small crystals began to form; the solution now solidified to a mass of crystals, and, after four recrystallizations, gave a white product, which melted sharply at 153°–154°. This process was repeated with solutious of rosin, both in dilute and in strong alcohol; they were found to darken rapidly and to develop considerable heat; at the same time there was formed a dark viscous substance, which was very difficult to remove in subsequent crystallizations. To avoid this, a very thorough cooling with a freezing-mixture was necessary. The anise-like odor mentioned by Flückiger was plainly noticeable during this operation.

One hundred grams "white rosin" were dissolved in 700 cubic centimeters of 70 per cent. alcohol with heat; the solution was filtered, cooled, and placed in a freezing-mixture, and dry[1] hydrochloric acid gas passed through. A thick oily layer separated in about twenty minutes, and gradually became crystalline; the crystals, however, were enclosed in a brown amorphous mass. The gas was allowed to pass for about one hour. The precipitate was filtered with suction, washed with alcohol of increasing dilution, and finally with sufficient water to remove all hydrochloric acid. The crude product was dissolved in 100 cubic centimeters of 95 per cent. alcohol, water added with stirring just to the point of cloudiness, and allowed to cool. In the next crystallization, less water was used for di-

[1] The gas is dried in order to avoid further dilution of the rosin solution.

lution, and the third was made from methyl alcohol. The product was slightly yellowish in color, had a melting-point of 158°–159°, and gave the following results on analysis :

0.2261 gram substance gave 0.2022 gram water and 0.6546 gram CO_2, corresponding to

	Per cent.
Hydrogen	9.94
Carbon	78.96

Three further crystallizations from methyl alcohol gave good white crystals having the same melting-point :

0.2590 gram of this substance gave 0.2309 gram water and 0.7592 gram CO_2, accordingly,

	Per cent.
Hydrogen	9.91
Carbon	79.03

A second analysis gave for 0.2078 gram substance, 0.1847 gram H_2O and 0.6011 gram CO_2.

	Per cent.
Hydrogen	9.87
Carbon	78.89

The following molecular weight determination was made by the boiling-point method : 0.3152 gram substance dissolved in absolute ether (17.221 grams) caused an elevation of 0°.132 in the boiling-point; hence the molecular weight equals 293 (K = 2110). By the freezing-point method, 0.4011 gram substance dissolved in 28.645 grams glacial acetic acid caused a lowering of 0°.133 in the freezing-point, which is equivalent to $\mu = 266$ (K = 3880).

Fifty grams "Black Rosin" were dissolved in 100 cubic centimeters of 95.5 per cent. alcohol, diluted with 20 cubic centimeters of water; the solution was filtered, and hydrochloric acid gas passed, until the beginning of crystallization. Violent stirring now completed the crystallization. The precipitate, which was dark in color, was filtered by means of suction, washed, and eight recrystallizations made. The final product had a melting-point of 154°–155°, was slightly yellowish in color, and was shown to be impure by the benzol and hydrochloric acid test :

0.1982 gram substance gave, on analysis, 0.1761 gram H_2O and 0.5728 gram CO_2.

	Per cent.
Hydrogen	9.87
Carbon	78.81

Fifty grams "Window Glass Rosin" were dissolved in 150 cubic centimeters 95 per cent. alcohol and dry hydrochloric acid gas passed in. Much heat was evolved, and large quantities of the usual brown by-products were formed. The mass was filtered and washed as usual. Five crystallizations were made from methyl alcohol and one from glacial acetic acid. The latter was washed with alcohol and the crystals dried over sulphuric acid in vacuum. The melting-point was

0.2239 gram of this substance gave, on analysis, 0.1944 gram H_2O and 0.6483 gram CO_2, corresponding to

	Per cent.
Hydrogen	9.65
Carbon	78.98

0.3400 gram of the same substance, dissolved in 33.332 grams glacial acetic acid, depressed the freezing-point 0°.138, corresponding to a molecular weight of 287 (K = 3880).

This method gives a pure product, with fewer crystallizations, than the method first employed, and in a much shorter time. However, not only is the objectionable by-product mentioned above very difficult to separate, but the product is generally lumpy, and the original rosin is, therefore, not completely hydrolyzed, but is left partly in an amorphous condition. It seemed necessary then to limit the amount of hydrochloric acid introduced, and to use some means of mechanical agitation to prevent the formation of lumps. To this end, some hydrochloric acid, 1.20 sp. gr., diluted with twice its volume of alcohol, was added to a solution of rosin in 95 per cent. alcohol contained in a bottle. The quantity of hydrochloric acid added was such that the water it contained would dilute all the alcohol present to about 75 per cent. The bottle was now wired to the chuck of a lathe and agitated for one hour. The abietic acid separated in the form of a finely divided crystalline powder. It was subsequently found that a very much

smaller quantity of hydrochloric acid would suffice to give a good precipitation, and, of course, in this case the obnoxious by-products were smaller in quantity.

Other mineral acids may be used instead of hydrochloric;[1] but this was found preferable to sulphuric or nitric. The chief difficulty in the preparation of pure abietic acid is not in the hydrolization of the anhydride, but in the separation of the amorphous by-products (terpenes and their oxidation products). The addition of a small quantity of hydrochloric acid greatly diminishes the solubility of abietic acid in alcohol, while that of the amorphous residue is, if anything, increased. It may be that pure abietic acid is not affected by hydrochloric acid in alcoholic solution. This is the basis of Twitchell's method for the determination of rosin. To a solution of purified abietic acid in alcohol was slowly added half its volume of hydrochloric acid, which caused an immediate separation. This was allowed to stand two months, when the crystals were filtered and washed; there was no change in the appearance of the crystals nor in melting-point. The mother-liquor was yellow, but this color was due to the action of hydrochloric on a small quantity of impurity still remaining.

The color produced in this way was used as a test for the presence of impurities in specimens of abietic acid. A small quantity of the latter is dissolved in 5 cubic centimeters of benzol in a test-tube. Five cubic centimeters hydrochloric acid, 1.20 sp. gr., are added and thoroughly shaken together. Any impurity present will give a brown to a yellow color to the lower layer; this is a very delicate test.

One hundred and fifty grams "White Rosin" were dissolved in 300 cubic centimeters hot 95 per cent. alcohol. The solution was filtered and allowed to cool. It was now violently agitated by means of a mechanical stirrer, while a mixture of 20 cubic centimeters of hydrochloric acid and 40 cubic centimeters of alcohol was slowly added. The solution grew cloudy and small oily drops separated. In about forty-five minutes,

[1] Mach used sulphuric acid in a similar manner for a preparation whose analysis approximated closer than any other to the theoretical requirement for $C_{19}H_{28}O_2$.

the solution had crystallized to a thick, creamy consistency, the agitation preventing the formation of any lumps and consequent occlusion of mother-liquor. The mass was filtered by means of suction, washed with very little dilute alcohol and much water. The dried product was plainly crystalline in character, of a light straw-color and weighed 112 grams. The melting-point at this stage was 140°–143°. After two crystallizations from ethyl alcohol and three more from methyl alcohol, the melting-point was 159°–161°. In the second and third crystallization, 2 per cent. by volume of hydrochloric acid was added to the hot solution.

0.2421 gram of the final product, dried over sulphuric acid in vacuum gave 0.2097 gram water and 0.7024 gram CO_2.

	per cent.
Hydrogen	9.63
Carbon	79.11

0.2143 gram of the same substance gave 0.1908 gram water and 0.6209 gram CO_2, corresponding to

	Per cent.
Hydrogen	9.89
Carbon	79.02

Two molecular weight determinations were made by the freezing-point method. 0.3750 gram substance, dissolved in 17.976 grams glacial acetic acid, depressed the freezing-point 0°.288 ; $\mu = 281$.

0.6303 gram substance in 22.243 grams glacial acetic acid gave a depression of 0°.364 ; $\mu = 302$.

300 grams "Window Glass Rosin" were dissolved in 300 cubic centimeters of hot 95 per cent. alcohol. The solution was filtered, cooled, and then violently agitated, while a mixture of 35 cubic centimeters of hydrochloric acid and 70 cubic centimeters of alcohol was slowly added. In about forty minutes, the solution had solidified to a crystalline mass. This was filtered and washed, as in the above preparations. This product, when dry, weighed 245 grams, and had a melting-point of 144°–148° ; it was, however, somewhat darker in color than the preceding one. It was now recrystallized from alcohol : a second and third crystallization were made with the aid of

hydrochloric acid and three more with methyl alcohol. This product was white and gave only a trace of color when tested for impurities as above described.

0.2762 gram of the dry substance gave, on analysis, 0.2435 gram water and 0.8021 gram CO_2.

	Per cent.
Hydrogen	9.80
Carbon	79.21

0.2177 gram gave 0.1902 gram water and 0.6313 gram CO_2.

	Per cent.
Hydrogen	9.71
Carbon	79.05

Four molecular weight determinations were made as follows, using glacial acetic acid and the freezing point method:

Gram substance.	Grams solvent.	Depression.	Molecular weight.
0.4307	23.0675	0.262°	277
0.3241	20.754	0.206°	294
0.4698	22.687	0.275°	292
0.2695	24.302	0.156°	276

To 50 grams "Gum Thus" dissolved in 100 cubic centimeters of alcohol were added 10 cubic centimeters of hydrochloric acid in 20 cubic centimeters of alcohol. The formation of crystals from this resin was very much slower in this process. After filtering and washing as usual, five crystallizations were made from methyl alcohol.

0.1946 gram of the dry substance gave 0.1716 gram H_2O and 0.5643 gram CO_2; hence,

	Per cent.
Hydrogen	9.77
Carbon	79.09

A molecular weight determination, made by the boiling-point method, resulted as follows: 0.7772 gram of this substance raised the boiling-point of 17.843 grams glacial acetic acid 0.357°; $\mu = 309$.

In the accompanying table will be found a list of the analytical results and of the molecular weights obtained. The average for twelve determinations of carbon and hydrogen

(omitting the analyses from the preparations of "Black Rosin," which were shown to contain much impurity by the color test) gives 9.80 per cent. hydrogen and 79.01 per cent. carbon. The various products obtained show sufficient agreement to prove their identity. The last method of preparation employed seems to give products of the greatest purity, and their analysis gives a somewhat higher carbon content. The molecular weight determinations show considerable variation.

TABLE OF ANALYTICAL RESULTS AND MOLECULAR WEIGHT DETERMINATIONS.

Preparation.	Hydrogen.	Carbon.	Molecular weight.
1. Maly's method, "White Rosin"	9.83	78.83	274, 303
2. " " " "	9.70	78.91	274, 303
3. " " "Black Rosin"	9.86	78.66	
4. " " "Gum Thus"	9.87	78.98	272
5. Flückiger's method, "White Rosin," 3d crystallization	9.94	78.96	293, 266
6. Flückiger's method, "White Rosin," 6th crystallization	9.91	78.03	293, 266
7. Flückiger's method, "White Rosin," 6th crystallization	9.87	78.89	293, 266
8. Flückiger's method, "Black Rosin"	9.87	78.81	
9. " " "Window Glass Rosin"	9.65	78.98	287
10. Direct addition of HCl to solution of "White Rosin"	9.63	79.11	281, 302
11. Direct addition of HCl to solution of "White Rosin"	9.89	79.02	281, 302
12. Direct addition of HCl to solution of "Window Glass Rosin"	9.80	79.21	277, 294 292, 276
13. Direct addition of HCl to solution of "Window Glass Rosin"	9.71	79.05	277, 294 292, 276
14. Direct addition of HCl to solution of "Gum Thus"	9.77	79.09	309
Average excluding Nos. 3 and 8, which were shown to contain inpurities	9.80	79.01	286
Theory for $C_{19}H_{28}O_2$	9.73	79.16	288

Hence the formulas proposed by Unverdorben ($C_{40}H_{60}O_4$, $\mu = 604$), by Trommsdorff and Rose ($C_{40}H_{64}O_4$, $\mu = 608$), and by Maly $C_{44}H_{64}O_5$, $\mu = 672$) are untenable. The other proposed formulas require the following composition and molecular weights:

The formula of Perrenond, Dietrich and Ducummun, $C_{10}H_{14}O$, requires 80.0 per cent. carbon and 9.33 per cent. hydrogen and a molecular weight of 300; *i. e.*, if abietic were $2(C_{10}H_{14}O)$.

The formula of Siewert and Strecker, $C_{20}H_{30}O_2$ (molecular weight = 302), requires 79.47 per cent. carbon and 9.94 per cent. hydrogen.

The only other possible formula (excepting that of Mach) whose composition approaches closely to the result of the above analyses, and which is within the limits of the molecular weight determinations made, is $C_{18}H_{26}O_2$, requiring 78.83 per cent. carbon and 9.49 per cent. hydrogen.

Finally, Mach's formula requires a molecular weight of 288 and a composition of 79.16 per cent. carbon and 9.73 per cent. hydrogen.

The results obtained in this work are accordingly expressed most exactly by the formula $C_{19}H_{28}O_2$.

PART III.

SALTS OF ABIETIC ACID.

Many salts of this acid have been described, and their metallic content determined; the results obtained show a great disparity, but have, nevertheless, been frequently used as a proof or even the basis of some of the proposed formulas. The original acid worked with was, in general, impure, and the products obtained were merely amorphous mixtures. Metallic abietates are made by double decomposition of metallic salts and alkali abietates. The latter are not readily obtained in a pure condition; only two observers have described them as crystalline. Maly described them as amorphous, and considered that this distinguished them from the salts of pimaric acid. Now, as will be seen below, neutral salts, even when pure, will, in the presence of water, quickly hydrolyze to an acid salt and free alkali, the former precipitating from solution because of its insolubility. To keep a neutral salt in solution, an excess of alkali is necessary, which, in a double decomposition, will precipitate metallic hydroxide; on the other hand, too large an excess will salt out alkali abietate. These are not conditions that will give pure salts.

It might be thought that recrystallization would remove the contaminants, but here again we meet with an hydrolysis of even a metallic salt, probably to acid salts, or free acid and metallic hydroxide. This process seems to be hastened by the action of sunlight (see page 42). Even Mach, whose salts were made with the greatest care, and whose analytical results approach closely to the theoretical percentages, admits that they cannot be accepted as a support for his formula.

The description of a few salts of abietic acid, given below, will give some idea of the difficulties met with in their preparation and purification. It is probable, however, that conditions may be found under which pure crystalline salts may be obtained; this work is not by any means concluded, and a more complete study of these salts will be undertaken with the view of obtaining further evidence for the formula proposed,

and of ascertaining the changes they undergo in the ordinary analytical and technical processes.

POTASSIUM SALTS.

Neutral Salt, $C_{19}H_{27}KO_2$

This salt is prepared with great difficulty, because of the facility with which it will revert to the acid salt. Its preparation requires digestion of the acid with potassium hydrate, or carbonate, for a long time, with complete absence of water. Mach used the carbonate, and obtained a salt which contained 12.21 per cent. potassium.[1] A neutral salt was made by this method, as follows:

Twenty grams pure abietic acid and 5 grams pure dry potassium carbonate were covered with 200 cubic centimeters of absolute alcohol and 100 cubic centimeters of ether, in a flask connected with a return condenser, and boiled for 210 hours.[2] An amorphous precipitate formed at first, but in the course of boiling, it went almost completely into solution. The product was finally filtered hot to remove the slight excess of potassium carbonate, was concentrated slightly by boiling, and allowed to cool. An amorphous mass separated, which, after filtration, was crystallized from alcohol and ether. The crystals were almost white, needle shaped, and melted at 143°. The potassium content was determined by burning in a platinum crucible with concentrated sulphuric acid, to which was occasionally added a few drops of nitric acid. Great care was necessary in this operation to avoid loss by foaming over. When the carbon had been completely oxidized, more sulphuric and nitric acids were added to reconvert any reduced sulphide to sulphate; this was evaporated, and the residue care-

[1] This is the average of three determinations which gave respectively 12.09, 12.25, and 12.30 per cent. potassium; these results he obtained by weighing the potassium carbonate remaining after a combustion for carbon and hydrogen.

[2] This preparation and others like it were heated on an air-bath made of an asbestos-lined box containing four 20 candle-power incandescent lamps. The top of the condenser was closed with a calcium chloride tube. In this way the preparation boiled fifteen hours per day for over two weeks without requiring any attention.

fully ignited. 0.4227 gram substance treated in this way gave 0.1102 gram potassium sulphate; this equals 11.70 per cent. potassium. The theoretical requirement for $C_{19}H_{27}KO_2$ is 11.96.

A better product was obtained by using potassium hydrate instead of the carbonate.

Eight grams potassium hydrate were dissolved in 150 cubic centimeters of absolute alcohol. Fifty grams pure abietic acid, dissolved in 100 cubic centimeters of ether, were now added, and the mixture boiled under a return condenser. The solution was clear at first, but in a few hours a thick white curd was found, which again went almost completely into solution in the course of four or five days; on cooling at this time, a copious mass of crystals formed. The boiling was continued for 210 hours. A portion was removed, heated with a little more alcohol and ether to complete the solution, filtered, and allowed to crystallize. A second crystallization gave a product which was almost white; it melted at 149°, and was neutral in action toward phenolphthalein.

0.3427 gram of this substance, treated with sulphuric acid, as described, gave 0.0921 gram potassium sulphate, which is equal to 12.07 per cent. potassium. (Theory: 11.96 per cent.)

Mach's salt contains a small quantity of impurity, as shown by some analyses he made for carbon, hydrogen, and potassium. He ascribes this to an absorption of oxygen during the long process of boiling; however, three analyses give for oxygen (by difference) respectively, 10.41, 10.77, and 10.59 per cent.; while $C_{19}H_{27}KO$ requires 10.82 per cent. This evidently does not indicate an absorption of oxygen. His potassium determinations gave results somewhat higher than the theoretical; but the method he employed, *viz.*, weighing the residual potassium carbonate after a combustion for carbon and hydrogen, is not without objection.

The crystals are white, can be recrystallized from alcohol and ether, and are more soluble in hot than in cold water; the solubility in water is greatly increased by the addition of a small quantity of alkali, while a large quantity has a "salting-out" effect, and will cause a precipitation of the salt.

The solubility of the neutral salt was found to be as follows:

Solvent.	Percentage content of saturated solutions at 20°.	No. of parts solvent required.
Ether	1.8	55.6
Absolute alcohol	5.8	17.2
Water		about 30

When freshly prepared, neutral potassium abietate is boiled with water and a clear solution is at first obtained, which will rapidly give a copious flocculent precipitate of an acid salt, and liberate free alkali. This can be shown by the addition of a few drops of phenolphthalein. The reaction seems to take place as follows:

$$n + 1\ (C_{19}H_{27}KO_2) + nH_2O = C_{19}H_{27}KO_2{}_1nC_{19}H_{28}O_2 + nKOH$$

The salt produced will be described more fully in the next section, on the acid salt. On keeping the neutral salt from three to four months, it was found to have dimished in solubility and changed in other properties, no doubt due to a spontaneous decomposition.

Acid Potassium Salt, $C_{19}H_{27}KO_2$, $3C_{19}H_{28}O_2$

Abietic acid has a tendency to form an acid salt under almost any conditions; more strictly speaking, this is a neutral salt with several molecules of acid of crystallization. The salt that has been obtained consists of three parts of abietic to one of neutral salt; it was first described by Siewert, and subsequently by Mach. It is stable and very insoluble, and is not affected by the presence of some free alkali.

Following are the conditions under which this salt was observed to form:

1. A slight excess of potassium hydrate acting on a saturated solution of abietic acid in alcohol (95 per cent. or less).

2. A slight excess of potassium carbonate boiled with an alcoholic solution of abietic acid for several hours.

3. From the freshly-prepared neutral salt, by boiling its aqueous solution.

4. From the freshly-prepared neutral salt, by allowing its aqueous solution to stand twenty-four hours or longer.

5. From a solution of abietic acid in aqueous potassium hydrate, by carefully regulating the quantities used.

1. To a hot concentrated solution of abietic acid in 95.5 per cent. alcohol was added a slight excess of an alcoholic solution of caustic potash. On cooling, acicular crystals separated, which, when filtered and dried, were analyzed.

0.4807 gram substance gave 0.359 gram K_2SO_4 = 3.35 per cent. potassium. Theory for $C_{19}H_{27}KO_2$, $3C_{19}H_{28}O_2$ = 3.28 per cent. potassium.

A portion of the preparation for neutral salt was removed after boiling one day (see page 34). Needle-shaped crystals were obtained on cooling, which, on recrystallizing, filtering, and drying, were analyzed.

0.4190 gram substance gave 0.305 gram K_2SO_4 = 3.27 per cent. potassium. The melting-point was found to be 197° [1]

2. A saturated solution of abietic acid in 95.5 per cent. alcohol, was boiled one hour with an excess of dry, powdered potassium carbonate. The solution was filtered hot and a few cubic centimeters of ether added until cloudy. On cooling, good crystals were obtained.

0.6022 gram substance gave 0.0481 gram K_2SO_4 = 3.58 per cent. potassium.

In one case, potassium carbonate was shaken in a large test-tube with an excess of a dilute alcoholic solution of abietic acid. On standing one day, large crystals of abietic acid separated on the sides; after the third day, the tube was almost filled with long needles of the acid salt.

3. Some freshly-prepared neutral potassium abietate was dissolved in cold water, and a few drops of phenolphthalein added — no color. On boiling violently, a copious, white, curdy precipitate formed and the solution reddened. The precpitiate was filtered and recrystallized twice from alcohol and ether. The melting-point was 187°.

0.6282 gram substance gave 0.0511 gram K_2SO_4 = 3.65 per cent. potassium. Theory for $C_{19}H_{27}KO_2$, $3C_{19}H_{28}O_2$ = 3.28 per cent. potassium. This is evidently the acid salt, and its formation may be expressed as follows:

$$4C_{19}H_{27}KO_2 + 3H_2O = C_{19}H_{27}KO_2,\ 3_{19}CH_{28}O_2 + 3KOH.$$

[1] Mach's acid salt melted at 183°.

All attempts to determine the amount of alkali liberated were futile, because of the uncertain action of phenolphthalein as indicator. The salt thus obtained is but very slightly soluble in water, and the presence of a small quantity of free alkali seems to exert no influence. This reaction probably expresses what takes place on dissolving and diluting a rosin soap, which is principally in the condition of a neutral salt, owing to the excess of free alkali used, and the concentrated condition of the solution from which it was made. It has been shown[1] that the detergent value of an ordinary soap is due to the liberation of free alkali by the hydrolytic action of water, and that this action is increased with the quantity of water used, and decreased with the presence of free alkali. With the potassium abietate, this is evidenced by the separation of the acid salt because of its great insolubility.

This reaction would, it seems, also explain the different results obtained in determining saponification figures for some resins, according to whether hot or cold solutions are used. It is known[2] that these figures are always highest when obtained in a cold solution, and vice versa. In a hot solution, the tendency is to form the acid salt, and consequently less alkali is necessary to reach the neutral point with the indicators ordinarily used.

Siewert's acid salt corresponds to this one in composition. On boiling this salt, he says it decomposes to the free acid (sylvic acid) and the neutral salt which goes into solution. No such change was observed with the acid salts of abietic acid, obtained by any of the methods described.

Duvernoy obtained crystalline neutral and acid salts of pimaric acid. The acid salt has the composition $C_{20}H_{29}KO_2$, $2C_{20}H_{30}O_2$. On boiling a neutral salt of this acid, he says he obtained the acid salt, but gives no data in support of this contention.

[1] Alder Wright, Jour. Soc. Arts, 23, 1885; Thorpe's "Dictionary of Chemistry," III, p. 412. A tallow-resin soap which he examined liberated 1.7 per cent. of the alkali, originally present, on adding 10 parts water, and 5.6 per cent. on adding 150 parts.

[2] K. Dietrich: Ch. Rev. f. Fett u. Harz, Ind. 1897, p. 1, et seq.

4. A solution of freshly-prepared acid salt, to which a few drops of phenolphthalein had been added, was allowed to stand twenty-four hours. The solution had become red, and a precipitate had formed, which was filtered, dried, and analyzed. 0.3794 gram substance gave 0.0353 gram K_2SO_4 = 4.17 per cent. potassium. The conversion to acid salt was evidently incomplete.

Ten grams pure abietic acid were covered with 1.5 grams potassium hydrate dissolved in 400 cubic centimeters of water. This was agitated and then allowed to stand without disturbance for three or four hours at 50°–60°. A scum of white needle-shaped crystals, imbedded in much gelatinous matter, had collected on the top of the solution and on the sides of the beaker. The solution was now boiled, upon which a dense precipitate formed, which had a silky texture, and could be drawn out into long threads — the same appearance as the crystallized acid salt when boiled with water. On filtering, recrystallizing from alcohol and ether, and drying, the following analytical results were obtained :

0.5946 gram substance gave 0.0409 gram K_2SO_4, = 3.09 per cent. potassium.

Properties of the Acid Salt.—This salt, when dry, is a white felt-like mass, consisting of fine acicular crystals, which melt at 197°.[1] As already stated, it is very insoluble, and not affected by a slight excess of alkali. The following solubility determinations have been made :

Solvent.	Percentage content of a saturated solution at 20°.	No. of parts solvent required for solution.
Ether	2.7	37.03
Equal parts alcohol and ether	9.5	10.5
Alcohol, absolute	31.3	3.2
" 95.5	3.8	26.31
" 70.0	3.7	27.03
Benzol	4.08	24.51
Petroleum ether (hot)	0.98	102.00

[1] Mach found the melting-point of his salt to be 183°.

SODIUM SALTS.

A crystalline neutral sodium salt can be obtained which is similar to the potassium salt.

Three and a half grams sodium hydrate were heated with 75 cubic centimeters absolute alcohol, and to this was added a solution of 25 grams abietic acid in 50 cubic centimeters ether and 25 cubic centimeter absolute alcohol. The mixture was heated in a flask connected with a return-condenser sealed by a calcium chloride tube, for 210 hours. A copious precipitate formed, which only partially dissolved during boiling. On cooling, acicular crystals formed which were yellowish in color.

0.3972 gram of the dry substance gave 0.0981 gram Na_2SO_4, corresponding to 8.00 per cent. sodium. Theory for $C_{19}H_{27}NaO_2$ = 7.42 per cent. sodium.

After three crystallizations the salt was white in color. Two analyses resulted as follows:

Substance. Gram.	Na_2SO_4. Gram.	Sodium. Per cent.
0.5339	0.0893	5.42
0.4962	0.0826	5.39

This corresponds neither to $C_{19}H_{27}NaO_2$ nor to $C_{19}H_{27}NaO_2$, $3C_{19}H_{28}O_2$, which requires 1.96 per cent Na. It is evident that here again an hydrolysis has taken place and the product is probably a mixture of the neutral salt, and one or more acid salts.

On boiling a solution of the neutral sodium salt containing a slight excess of alkali a precipitate is obtained.

0.1750 gram of the dried salt gave 0.0191 gram Na_2SO_4 = 3.54 per cent. sodium.

A sodium salt, $C_{19}H_{27}NaO_2,C_{19}H_{28}O_2$, corresponding to the ammonium salt obtained by Mach ($C_{19}H_{27}NH_4O_2,C_{19}H_{28}O_2$) requires 3.85 per cent. sodium.

The neutral salt is crystalline; that obtained after the third crystallization melts at 216°. The following solubility determinations were made with this salt.

Solvent.	Percentage content of a saturated solution at 20°.	Parts solvent required for solution.
Ether (hot)	0.22	456.00
" 20°	0.21	480.00
Petroleum ether (hot)	0.21	480.00
Alcohol, absolute	2.00	50.00
" 95.5	16.86	5.93
Water (freshly prepared salt)	11.69	8.55
Water (salt that had been standing three months	10.16	9.84

Ammonium Salt.

Mach obtained a crystalline ammonium salt and removed thereby the supposed distinction between abietic and pimaric acids. He prepared the salt by adding ammonium carbonate to an alcoholic solution of abietic acid, and also by passing a mixture of ammonia gas and carbon dioxide into such solution. His analytical results approach closely to the requirements for $C_{19}H_{27}NH_4O_2, C_{19}H_{28}O_2$. A crystalline ammonium salt was obtained by the following method:

A solution of abietic acid in alcohol and ether was boiled with a return-condenser while a slow current of ammonia gas (dried by passing over soda-lime) was passed through. The gas was passed into the boiling solution for one day; the product was allowed to cool and the gas passed the same length of time through the cold solution. A crystalline salt was obtained, which, after the second crystallization, had but a slight tinge of color, and was neutral in reaction and in smell. The addition of potassium hydrate to the salt liberated ammonia. On adding water to an alcoholic solution of this salt and allowing to stand several days, crystals were found to separate. On examining such crystals they were found to be triclinic plates, to rotate the plane of polarization, and to melt at 157°; accordingly they are free abietic acid. A complete hydrolysis evidently takes place with the separation of ammonia and free abietic acid. The dry salt, when kept any length of time, will evolve ammonia to a noticeable extent; this decomposition seems to be more rapid in direct sunlight.

Several attempts were made to determine the ammonia content by treating with a known excess of standard acid and titrating back with standard alkali. The results were variable and gave no decisive clue to the composition of the salt. One of the determinations made is here given :

1. 0.6392 gram substance was treated with 10 cubic centimeters tenth-normal hydrochloric acid and 50 cubic centimeters water. After digesting one hour, the product was filtered, washed, and titrated with decinormal potassium hydrate. 5.36 cubic centimeters KOH were required, corresponding to 5.25 per cent. NH_4.

$C_{19}H_{27}NH_4O_2$ requires 8.78 per cent. NH_4.

$C_{19}H_{27}NH_4O_2, C_{19}H_{28}O_2$ requires 3.09 per cent NH_4.

OTHER SALTS OF ABIETIC ACID.

By the use of the potassium salt for double decomposition, abietates were obtained of the following metals : Barium, calcium, magnesium, zinc, iron, manganese, chromium, and silver. Some of these were prepared in aqueous and some in alcoholic solution. The products were all amorphous ; such analyses as were made for metallic content gave results that were quite close to the theoretical requirements for neuttal salts.

It has been observed that crude metallic resinates vary in solubility under the influence of sunlight.[1] The same phenomenon was observed with the pure salts obtained, notably those of zinc and magnesium. Some zinc salt, which formed a clear solution in benzol, was exposed to sunlight in a shallow layer for two days (protected, of course, from laboratory fumes). Now on treating with benzol a white residue remained which dissolved in acid with slight effervescence, and was shown to be zinc hydrate with a small quantity of carbonate. An excess of the unexposed salt, treated with benzol, gave a solution which contained 10.7 per cent. of its weight of substance, while after exposure a similar solution (after decanting from

[1] Müller-Jacobs: Ztschr. angew. Chem., 1890.

the insoluble residue described) contained 55.1 per cent of substance.

There has evidently been formed free abietic acid or an acid salt more soluble in benzol. However, no crystals of abietic acid could be obtained from this solution. Some of the silver salt was exposed to light, treated with alcohol and ether, filtered, and diluted with water. In the amorphous mass obtained, crystals of abietic acid could be identified by the use of the microscope and polarized light.

Maly observed that metallic abietates, which had been kept some time, differed in properties from those freshly prepared; he found that some salts, especially that of barium, gained in weight. This he ascribed to oxidation. He prepared a zinc salt by double decomposition, which contained 11.02 per cent. Zn [$(C_{19}H_{27}O_2)_2Zn$ requires 10.2 per cent. Zn)]. On dissolving in alcohol and precipitating with ether, and repeating this treatment several times, a product was finally obtained which contained 17.11 per cent. zinc.

Colored Resinates.

Closely related to the salts just discussed are the colored resinates described by Müller-Jacobs.[1] They are prepared by adding a basic organic dyestuff to a dilute rosin soap, and then precipitating by the addition of a solution of metallic salt. The product obtained has retained the color of the dyestuff, is insoluble in water, slightly soluble in alcohol, but readily soluble in benzol, turpentine, and most oils and fats. Perhaps the most interesting feature of these products is their sensitiveness to light. This property has made them the basis of a photo-engraving process.[2]

The colored resinates seem to be double salts of the metallic base and the color base with abietic acid. A large number were prepared and studied with the hope of getting some clue to their composition and the nature of the change they undergo through the influence of light. The products are complex and vary according to the conditions of their preparation. Deter-

[1] Ztschr. angew. Chem., 1889, p. 432; Ding. poly. J., 273, 139; Reimann's Färberzeit., 30, 1894.

[2] Müller-Jacobs: Ztschr. angew. Chem., 1890.

minations of their metallic content were made and it was attempted to find the percentage of colorbase by a series of colorimetric comparisons. The results obtained were unsatisfactory, but the work has not been completed and it is hoped that more decisive results will be obtained.

The remainder of this discussion will be limited to a few observations made with these products. There are several facts that point to a double salt structure for the colored resinates. It has already been seen that abietic acid has a tendency to form acid salts with the alkalies ; such salts have free carboxyl groups to unite with the basic color, and the great insolubility of the new product formed will cause its precipitation from aqueous solution. Warm solutions in which the tendency to form acid salts is greatest, give the best quality of resinate color. Cold solutions give irregular products and require larger quantities of metallic salt to precipitae them. To a cold solution of pure neutral potassium abietate were added solutions of rosanilin and zinc sulphate ; a small quantity of benzol soluble-colored salt was produced. A much larger yield was obtained when the solutions were heated or when the acid salt was originally used.

A solution of neutral potassium abietate was heated with some methyl violet. On cooling with ice a benzol-soluble salt was produced which contained potassium.

Some of the dry colored salt made from pure abietic acid was exposed to sunlight in a shallow layer. It had previously been washed until all water-soluble color was removed ; after exposure and treatment with water, a deep color was imparted to the latter, showing that free basic color had been produced. Other products of the decomposition could not be identified ; the action of light on the material in bulk, is slow. A thin film of the substance placed under a negative is sufficientiy exposed in from fifteen to thirty minutes, but in such case the quantity of material is too small to work with.

A saturated benzol solution of a zinc-rosanilin abietate prepared in diffused daylight, contained 12.1 per cent. of its weight of substance ; a similar solution of the same material, after ex-

posure to sunlight for one day, contained 1.6 per cent. of its weight of substance.

It was attempted to prepare simple salts of abietic acid with basic colors and with anilin, but none could be obtained.

Some experiments were made with the hope of utilizing the colored salts as a test for rosin (*e. g.*, in soap) and perhaps of devising a method of colorimetric determination.
Work in this direction will be continued.

CONCLUSION.

In the first part of this work further evidence was obtained for the anhydride structure of rosin. It was also shown that the anhydride will form on heating the acid, and that abietic acid cannot be looked upon as an oxidation product of turpentine.

Pure abietic acid was produced by an improved method. The examination of the products obtained confirmed in every respect Mach's formula, $C_{19}H_{28}O_2$.

Some new salts were made and some new tests applied. It was shown that the salts of abietic acid are decomposed by the action of water, and more rapidly when exposed to sunlight. The products of the decomposition were in some cases identified.

BIOGRAPHICAL.

Hermann A. Loos was graduated from the College of the City of New York in 1895, with the degree of Bachelor of Science.

1895–1897—Teacher in New York City public schools.

1895–1899—Teacher in New York City evening schools.

1896—Summer Course in Chemistry, New York University.

1897–1900—Attended under Columbia University Faculty of Pure Science.

1898—Received the degree of Master of Arts; Thesis: "The Electrolytic Determination of Zinc as Amalgam."

1898–1899—Instructor in Chemistry at the East Side Evening High School, New York City.

1899–1900—University Fellow in Chemistry.

Publications—"A Study on the Metallic Carbonyls and their Decompositions" (with V. Lenher), School of Mines Quarterly, 21, 182. "On the Decomposition of Nickel Carbonyl in Solution" (with V. Lenher). J. Am. Chem. Soc., 22, 114.